Nitrate-N Isotope Results and Interpretation

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Introduction

In May 2018, EPA conducted sampling at multiple locations in Wood and Juneau counties in Wisconsin up-gradient and down-gradient of Central Sands Dairy, LLC production area and land application fields. The purpose of the sampling was to identify potential manure contamination of ground water, surface water, and drinking water. EPA provided 87 samples to the University of Nebraska (UNL) Water Sciences Laboratory for ^{15}N-NO_3 and ^{18}O-NO_3 isotope analysis. UNL provided nitrate-N concentrations and stable isotope results for 71 of the 87 samples on June 11, 2018. EPA is requesting that UNL provide additional explanation and interpretation of the analytical results. This report will include the following:

- An explanation of the stable isotope analysis of nitrate, how it is measured, and how it may be applied in groundwater.
- A discussion of the expected ranges of nitrogen and oxygen isotope composition for nitrate due to sources and expected effects from denitrification using information from scientific literature.
- Plots of ^{15}N-NO_3 versus nitrate concentration for samples received compared to expected ranges based on sources and effect from denitrification.
- Plots of measured ^{18}O-NO_3 versus ^{15}N-NO_3 compared to expected ranges based on sources and effect from denitrification.
- Evaluation of any anomalous results.
- Evaluation of isotope results in the context of other water chemistry data.
- List of supporting references

Background on stable isotope analysis of nitrate

Nitrate (NO_3) is composed of multiple stable isotopes of nitrogen and oxygen, and the composition or proportion of these isotopes changes in a predictable way in surface and groundwater systems. Moreover, nitrogen from specific sources has been shown to have a unique isotope composition or "fingerprint" which has led to a number of studies investigating the utility of linking nitrogen sources to nitrate contamination. The conventional method for measuring and reporting the stable isotope composition uses a delta (δ) notation based on the following equation:

$$\delta(o/oo) = \frac{R_{sample} - R_{air}}{R_{air}} \times 1000$$

where "R" is the measured isotope ratio of the less abundant isotope over the more abundant isotope for a sample and standard (air). In the case of nitrogen, "air" or atmospheric nitrogen gas is used as the reference standard with a very constant ^{15}N composition of 0.366% (Junk and Svec, 1958). The reference for oxygen isotopes is standard mean ocean water (SMOW) with a $^{18}O/^{16}O = 2005.2$ ppm.

Measurement of Nitrate Isotopes

A number of methods for high precision stable isotope analysis of nitrate have been published over the past several decades. A recent mini-review discusses advantages and disadvantages of the most common approaches (Dai, Xie, et al., 2017). All methods require separation and

conversion of dissolved nitrate into gases that can be introduced into a high precision light gas stable isotope mass spectrometer. Early methods, such as those published by (Spalding, Gormly, et al., 1978) and used at the Water Sciences Laboratory until 2017, required multiple chemical conversions, labor-intensive steam distillation and high vacuum gas-phase oxidation to purified nitrogen (N_2) gas. While a proven technique, most analytical approaches use either ion exchange separation of nitrate, followed by high temperature conversion to nitrogen gas and carbon monoxide using an elemental analyzer ((Silva, Kendall, et al., 2000), or direct chemical (McIlvin and Altabet, 2005) or microbial (Casciotti, Sigman, et al., 2002) conversion to nitrous oxide (N_2O). The newer methods are faster, can be semi-automated and permit direct measurement of both nitrogen and oxygen isotopes in nitrate.

The method employed at the Water Sciences Laboratory uses a two-step chemical conversion of nitrate using alkaline Cd-reduction of dissolved nitrate to nitrite, followed by acidic reaction of nitrite with azide to produce nitrous oxide (N_2O). N_2O is purged and cryogenically trapped on an Isoprime Tracegas preconcentrator interfaced with a GVI isotope ratio mass spectrometer. Trapped N_2O is chromatographically separated from nitrogen gas, and ions with m/z =44, 45, and 46 are simultaneously separate and monitored on a multi-collector magnetic sector mass spectrometer. Standard nitrate solutions of from known, or isotopically-characterized nitrate are processed and analyzed in the same way as samples, and the results used for calibrating the mass spectrometer and determining. A working N_2O gas standard is measured between every sample and the ratios 44/45 and 44/46 converted to deltas (δ) using the instrument software.

Stable Isotope "Fingerprinting" of Nitrate
Nitrogen in commercial fertilizers (urea and anhydrous ammonia) has an isotope composition very similar to atmospheric nitrogen, and typically ranges from -6 to +6 per mil (‰)(Kendall, Elliott, et al., 2008). Extensive data collection and analysis of fertilizer sources has suggested that the isotope composition of the majority (~80%) of inorganic nitrogen fertilizer sources ranges between -3 and +3‰ (Michalski, Kolanowski, et al., 2015). In comparison, nitrogen from animal manure, sewage or biosolids tends to be enriched in the heavier ^{15}N isotope, especially after deposition and conversion to the highly volatile ammonia (Kendall, Elliott et al. 2008), and its range tends to be significantly higher, typically between +10 and +25‰. Oxygen isotopes in nitrate, may either originate from the oxygen in a commercial nitrate fertilizer (KNO_3 or $N_2H_4O_3$) or from oxygen atoms in the soil, air, and water during nitrification of ammonia. Because the oxygen isotope composition in air is relatively constant (+22 to +24‰), and the oxygen isotope composition of water changes in a predictable way (usually -5 to -20‰), it is possible to predict the oxygen isotope composition of soil nitrate formed by nitrification.

Both the nitrogen and oxygen isotope composition can be changed in nitrate by another process called microbial denitrification, changes nitrate to nitrite, nitrous oxide, and may eventually convert nitrate to nitrogen gas and water. Because the change in composition is predictable, simultaneous measurement of both nitrogen and oxygen isotopes can provide clues about the source(s) of nitrogen, timing of nitrification (nitrate formation), and whether denitrification has helped to remove any nitrate. As figure 1 indicates, however, the use of both nitrogen and oxygen isotopes for distinguishing sources of nitrate in groundwater can be complicated by multiple sources (atmospheric, manure, septic systems) and processes.
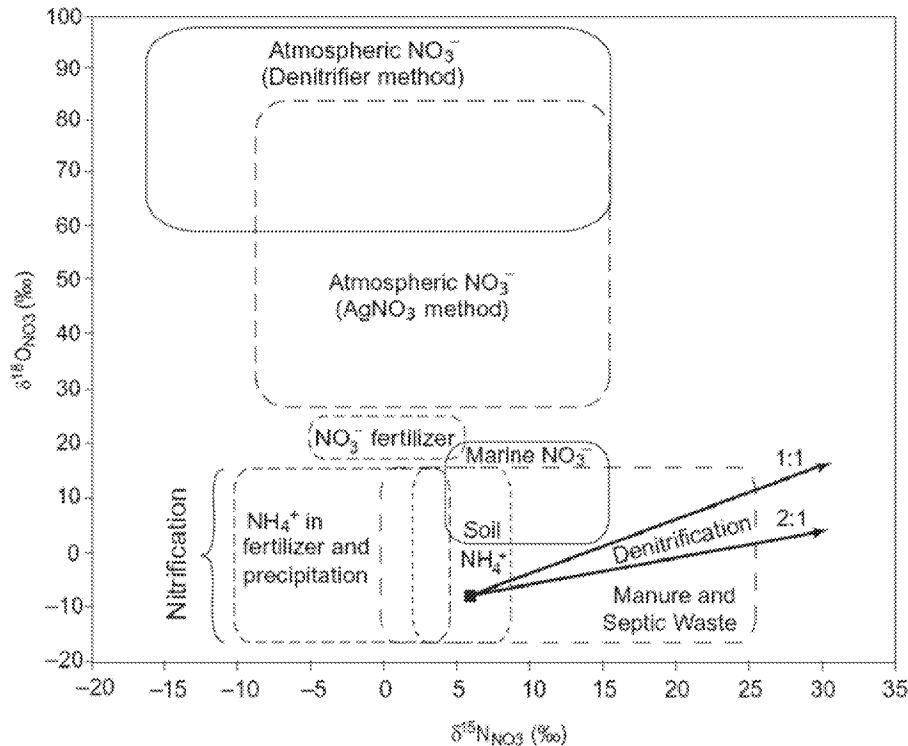
Figure 1. Expected variation of ^{15}N-NO_3 and ^{18}O-NO_3 from a variety of sources, along with the predicted trends due to denitrification (Kendall et al 2008).

Finally, interpretation of the measured isotope composition of nitrate in groundwater samples with respect to potential sources should include consideration of the expected ranges from sources, potential for mixing multiple nitrogen sources, and the possibility of changes in the isotope composition due to biogeochemical processes (Kendall and Aravena, 2000). While this is often challenging, comparing the measured isotope composition of nitrate with other parameters, such as dissolved oxygen, iron, chloride and alkalinity, can help support interpretations.

Trends from the Study Area Samples
Figure 2 shows the relationship between increasing isotope composition with groundwater nitrate concentrations of samples analyzed for this study. Denitrification of a single (organic or inorganic fertilizer) source can be indicated by an inverse trend between groundwater nitrate-N concentration and nitrogen-15 content of residual nitrate (Gormly and Spalding, 1979), especially with increasing depth. A single source of nitrogen is not indicated by the relationship between nitrate concentration and $\delta^{15}N$-NO_3.

Plots of the $\delta^{15}N$-NO_3N composition versus the natural log and inverse ($1/NO_3N$) concentrations can help distinguish between denitrification and simple mixing. Figure 3 shows the relationship between the natural log of nitrate-N concentrations (mg/L) versus $\delta^{15}N$-NO_3N composition of nitration. A log-linear trend between nitrate-N concentration and $\delta^{15}N$-NO_3N provides evidence supporting microbial denitrification as a factor controlling the isotope composition of groundwater nitrate (Kendall and Aravena, 2000). As noted above, biogeochemical transformation of nitrate can increase the nitrate-N

isotope composition and must be considered when interpreting nitrate isotope results. The correlation is weak, however, suggesting denitrification is not the only process contributing to enrichment of δ^{15}N-NO_3N.

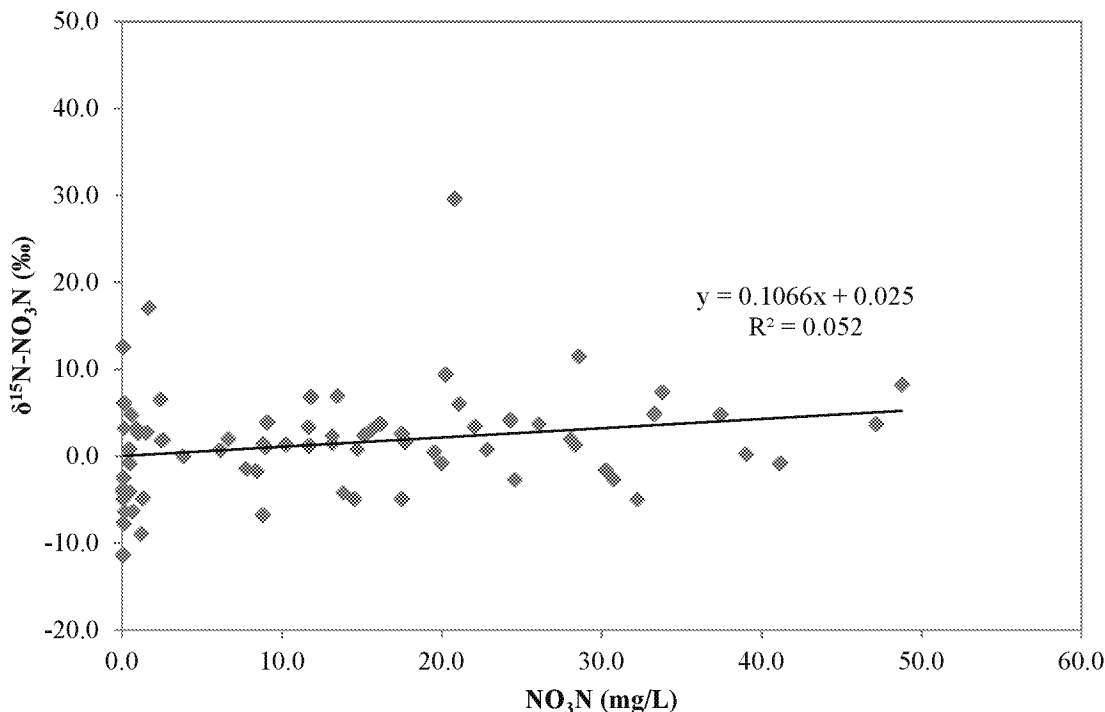*Figure 2. Correlation between δ^{15}N-NO_3N and groundwater nitrate concentrations. Trend line is consistent with an overall increase of nitrogen-15 isotope composition with increasing concentration.*

A plot of δ^{15}N-NO_3N versus δ^{18}O-NO_3N is shown in figure 5 together with expected ranges for nitrate resulting from nitrified commercial nitrogen fertilizer (anhydrous ammonia, urea, etc.), nitrate-N from manure and septic system effluent, and inorganic nitrate fertilizer sources. Only 1 sample plots in the isotope range inorganic nitrate fertilizers, while over 50% of the samples plot in the range expected for nitrification of commercial nitrogen fertilizer. Roughly one-third of the isotope results fall in the range expected for manure and septic system nitrogen, and several points are consistent with enrichment due to denitrification (Kendall, Elliott, et al., 2008).

Unusual or Anomalous Isotope Results
The majority of the nitrate isotope composition measured are consistent with ranges expected from nitrification of commercial nitrogen fertilizer or organic nitrogen sources. Denitrification of nitrate-N in the groundwater would be expected to shift both the δ^{15}N-NO_3N and δ^{18}O-NO_3N to more enriched values and several points are consistent with this enrichment. Samples from location "E" tend to have isotopically enriched nitrate, and also are lower in dissolved chloride and sulfate (Table 1). Nitrate from sample ID "E9a" (45' depth) had the highest measured δ^{15}N-NO_3 = +29.79‰ and is consistent with nitrogen from an organic source. Several samples had very low (negative) δ^{15}N-NO_3N results, ranging from -5 to -11.41‰. Negative, or depleted $\delta15$N-NO3N occurs during incomplete nitrification of soil nitrification. Significant depletion of

δ^{15}N-NO$_3$N can also occur during partial denitrification (Bates, Martin, et al., 1998, Kendall, Elliott, et al., 2008).

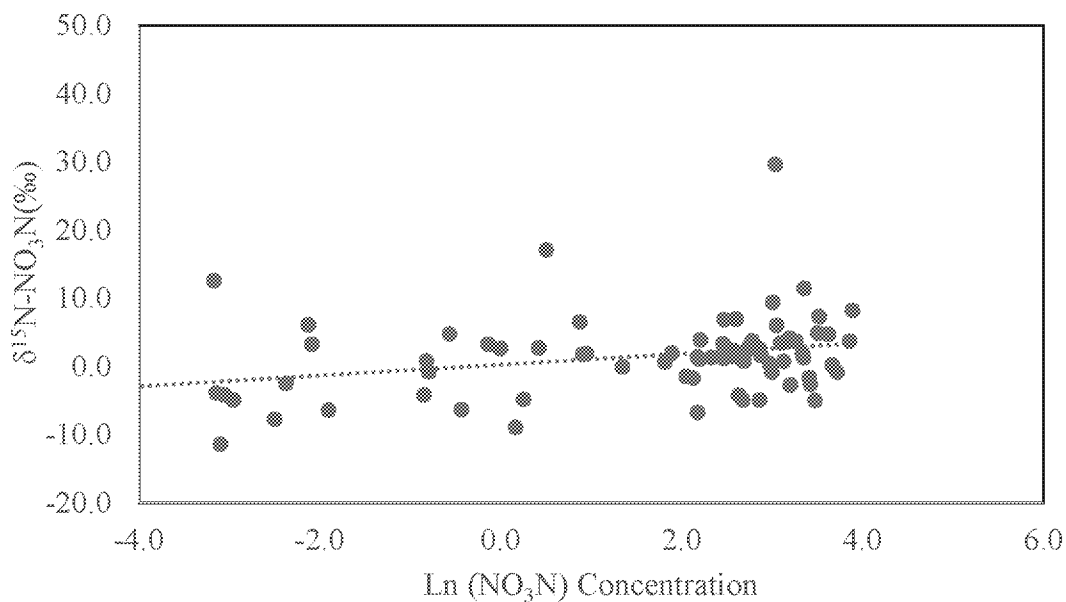*Figure 3. Trend of the natural log (Ln) of nitrate-N concentrations versus ^{15}N-NO$_3$ composition of nitrate. A linear trend is consistent with microbial fraction due to denitrification.*
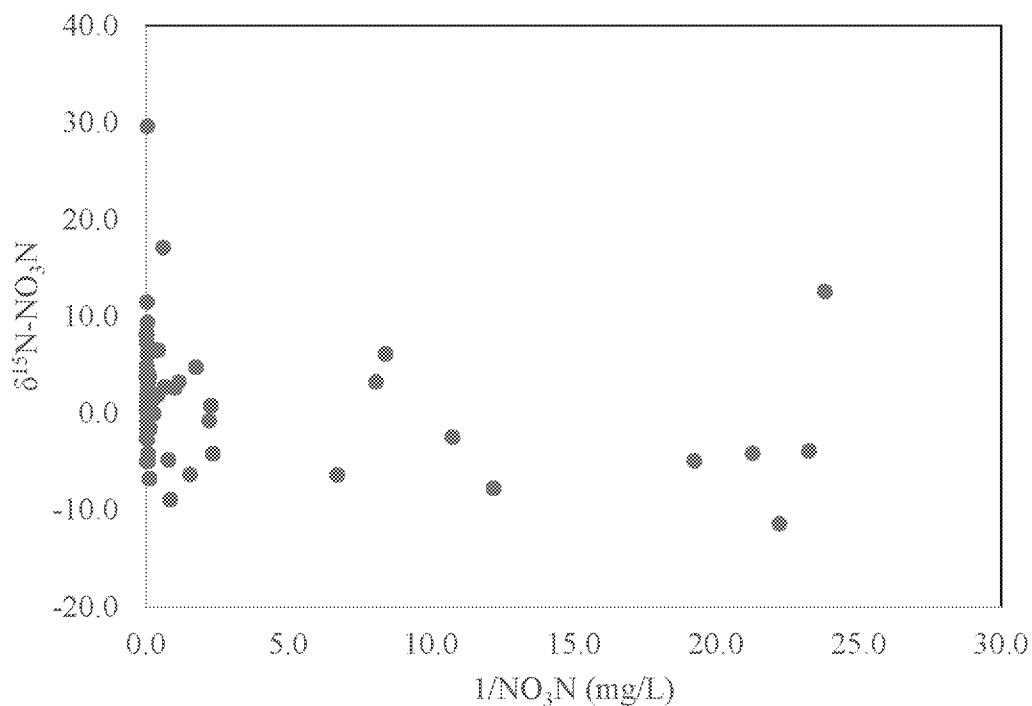

Figure 4. Trend of inverse nitrate concentration (1/NO3N) versus ^{15}N-NO$_3$N of nitrate. Simple mixing or dilution of a single source would be indicated by a linear correlation.
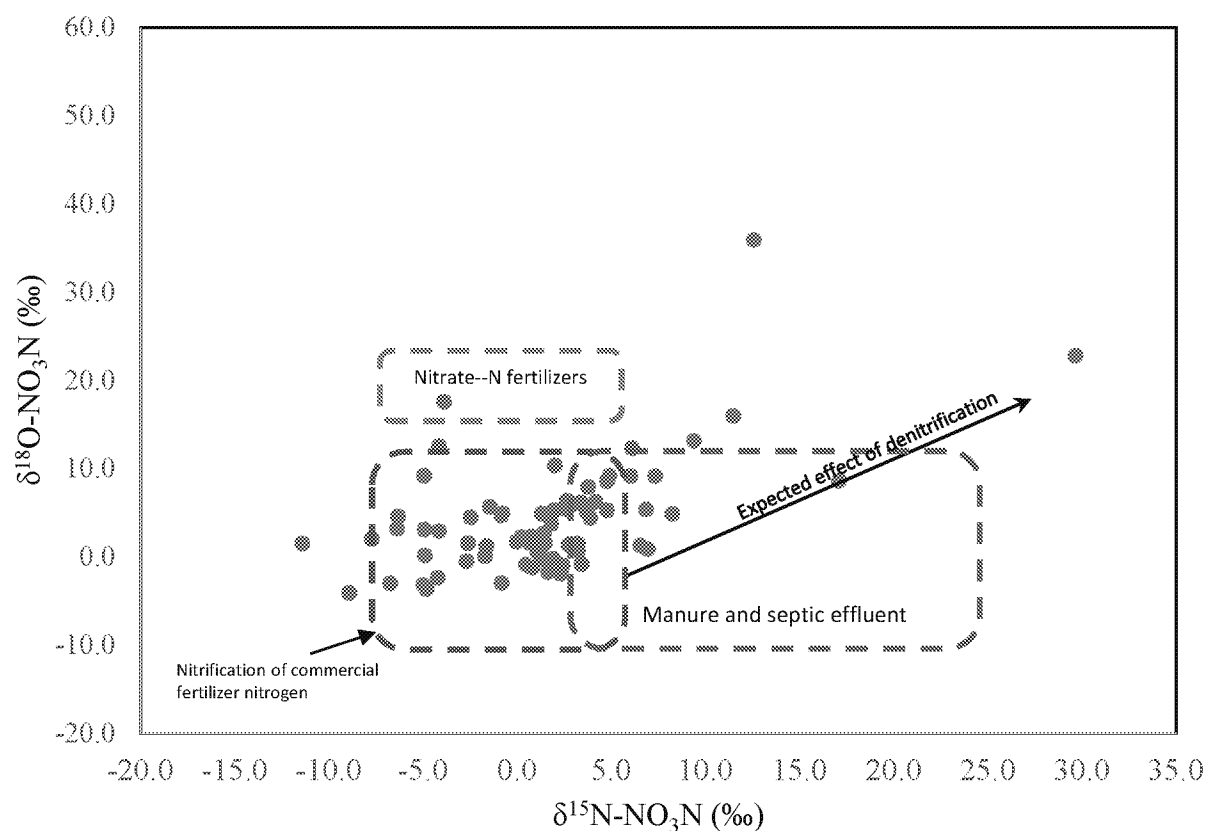
Figure 5. Measured δ¹⁵N-NO₃N versus δ¹⁸O-NO₃N compared to expected ranges from commercial fertilizer sources (dark blue dashed box), manure and septic sources (orange dashed box) and inorganic nitrate fertilizers (green box). Trend arrow of increasing δ¹⁸O-NO₃N and δ¹⁵N-NO₃N for enrichment due to denitrification. Ranges and arrow from (Kendall and Aravena, 2000).

Related Water Chemistry

A spreadsheet listing of related water chemistry data collected with these samples was received July 26th from Cheryl Burdett, including samples analyzed at EPA's Chicago Regional Laboratory. Selected results are included in Table 1 for direct comparison of nitrate isotope measurements with field measurements (pH, temperature, depth), nitrate-N concentrations, δ^{15}N-NO₃N, δ^{18}O-NO₃N, dissolved chloride, sulfate, ammonia-N, iron and manganese. Nitrate-N concentrations from field samples averaged 10.0±11.6, and concentrations higher than 10 tended to occur in deeper samples (>30') and in samples collected toward the end of the sampling event. Samples with higher nitrate concentration also tended to have elevated chloride, sulfate, ammonia-N and iron (Table 1). Elevated iron and ammonia-N concentrations are consistent with reducing conditions in groundwater likely to encourage microbial denitrification. Total organic carbon was measured but did not appear to show any trend with other parameters. There is a general positive correlation (R^2=0.67 of dissolved chloride with sulfate, and samples with high dissolved chloride tend to have lower δ^{15}-NO₃N characteristic of commercial nitrogen sources.

Literature Cited

Junk, G. and H.J. Svec. 1958. The absolute abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources. Geochim. Cosmochim. Acta 14: 234-243.

Kendall, C. and R. Aravena. 2000. Nitrate Isotopes in Groundwater Systems. In: P. G. Cook and A. L. Herczeg, editors, Environmental Tracers in Subsurface Hydrology. Springer US, Boston, MA. p. 261-297.

Kendall, C., E.M. Elliott and S.D. Wankel. 2008. Tracing Anthropogenic Inputs of Nitrogen to Ecosystems. Stable Isotopes in Ecology and Environmental Science. Blackwell Publishing Ltd. p. 375-449.

Michalski, G., M. Kolanowski and K.M. Riha. 2015. Oxygen and nitrogen isotopic composition of nitrate in commercial fertilizers, nitric acid, and reagent salts. Isotopes in Environmental and Health Studies 51: 382-391. doi:10.1080/10256016.2015.1054821.

Table 1. Summary of field parameter data, nitrate and nitrate isotope measurements, together with selected water chemistry data from EPA's Chicago Regional Laboratory.

Field Measurements						University of Nebraska					EPA R5 Laboratory					
Sample_ID	SampleDate_Time	pH_SU	Water_Temperature_C	Nitrate_Field_Test_mgl	Sample_Depth_from_Surface_ft	Sample_ID	NO3+NO2-N	Sample_ID	15N-NO3	18O-NO3	Sample ID	Chloride (mg/L)	Sulfate (mg/L)	Ammonia-N (mg/L)	Iron (ug/l)	Manganese (ug/l)
A1a	4/30/18 7:19	7.9	11.6	5	45	A1A	0.000	A1A	--	--	A1a	4.6	7.0	0.25	115.0	2.1
A2a	4/30/18 8:15	7.31	11.1	0	45	A2A	0.000	A2A	--	--	A1b	1.2	6.0	0.36	43.1	1.0
A2b	4/30/18 8:24	7.38	10.4	1	24	A2B	0.006	A2B	--	--	A2a	1.2	9.8	0.31	98.4	2.3
A3a	4/30/18 9:06	7.76	13	1	45	A3A	0.021	A3A	--	--	A2b	0.9	5.0	0.29	30.7	3.0
A3b	4/30/18 9:14	6.65	12.5	0	20	A3B	0.047	A3B	-4.15	12.52	A3a	0.8	8.8	U	51.6	2.3
A4a	4/30/18 9:58	6.55	12.8	2	45	A4A	0.568	A4A	4.76	5.27	A3b	0.8	6.4	U	81.4	2.5
A4b	4/30/18 10:09	6.09	12.2	4	20	A4B	0.124	A4B	3.23	0.70	A4a	1.0	26.5	U	38.3	0.8
B1a	4/30/18 10:51	7.04	13.2	0	45	B1A	0.018	B1A	--	--	A4b	0.5	10.7	0.25	30.7	1.5
B1b	4/30/18 10:58	6.57	12.5	0	20	B1B	0.043	B1B	-3.89	17.57	B1a	0.7	8.2	0.25	31.2	1.0
B2a	4/30/18 11:40	7.38	12	0	45	B2A	0.000	B2A	--	--	B1b	1.1	7.9	0.21	88.9	0.9
B2b	4/30/18 11:48	6.38	11.5	0	20	B2B	0.082	B2B	-7.73	2.04	B2a	2.8	8.8	U	82.4	1.6
B3a	4/30/18 12:29	6.42	13.4	5	45	B3A	1.284	B3A	-4.83	-3.64	B2b	0.5	5.1	U	39.1	0.6
B3b	4/30/18 12:36	6.25	12.5	2	20	B3B	0.000	B3B	--	--	B3a	19.5	26.3	0.62	35.0	3.6
B4a	4/30/18 13:10	6.77	15.5	50	45	B4A	17.473	B4A	-4.91	0.17	B3b	2.1	6.7	0.37	87.1	2.2
B4b	4/30/18 13:41	6.47	14.7	50	20	B4B	8.807	B4B	1.41	2.66	B4a	35.0	66.3	0.61	19.0	4.0
C3a	4/30/18 14:16	6.32	16.5	20	45	C3A	9.083	C3A	3.88	4.41	B4b	26.7	112.0	3.56	93.4	1.8
C3b	4/30/18 14:26	6.16	16.5	3	20	C3B	0.440	C3B	0.81	-1.22	C1a	0.7	7.8	U	14.0	1.2

Field Measurements						University of Nebraska					EPA R5 Laboratory					
Sample_ID	SampleDate_Time	pH_SU	Water_Temperature_C	Nitrate_Field_Test_mgl	Sample_Depth_from_Surface_ft	Sample_ID	NO3+NO2-N	Sample_ID	15N-NO3	18O-NO3	Sample ID	Chloride (mg/L)	Sulfate (mg/L)	Ammonia-N (mg/L)	Iron (ug/l)	Manganese (ug/l)
C1a	4/30/18 15:02	6.25	14.6	0	45	C1A	0.000	C1A	--	--	C1b	0.7	6.5	U	13.4	1.9
C1b	4/30/18 15:27	6.58	14.8	0	30	C1B	0.045	C1B	-11.41	1.50	C2a	34.4	29.2	0.25	12.9	4.0
C2a	4/30/18 16:06	6.05	15.6	50	45	C2A	22.807	C2A	0.75	2.30	C2b	3.3	15.7	0.81	53.9	9.5
A1b	4/30/18 7:32	6.9	9.8	3	20	A1B	0.052	A1B	-4.94	9.19	C3a	30.0	40.9	1.19	31.9	14.3
C2b	4/30/18 16:14	6.46	16.5	10	30	C2B	0.866	C2B	3.22	1.51	C3b	5.8	11.5	0.24	6.8	0.8
C5Aa	5/1/18 6:29	6.11	12.2	20	45	C5AA	13.147	C5AA	2.32	-1.91	C5Aa	38.8	90.4	0.6	15.9	3.9
C5Ab	5/1/18 6:43	6.64	12.1	50	30	C5AB	22.042	C5AB	3.42	-0.80	C5Ab	50.5	101.0	2.13	126.0	8.1
C6a	5/1/18 7:06	8.35	11.8	50	45	C6A	15.132	C6A	2.40	-0.95	C6a	43.5	54.7	0.71	21.1	9.6
C6b	5/1/18 7:15	6.8	12	50	30	C6B	11.703	C6B	1.19	0.79	C6b	29.5	88.9	3.96	54.8	10.7
C7a	5/1/18 7:48	8.28	14.2	50	45	C7A	19.503	C7A	0.45	-0.85	C7a	33.6	52.5	U	19.6	9.9
C7b	5/1/18 8:02	6.3	13.1	50	30	C7B	14.692	C7B	0.78	2.17	C7b	35.9	95.2	0.27	91.4	11.6
C8a	5/1/18 8:35	6.44	13.1	20	45	C8A	6.636	C8A	1.99	10.37	C8a	15.9	44.5	0.25	18.9	12.2
C8b	5/1/18 8:42	6.48	13.5	5	30	C8B	2.392	C8B	6.53	1.34	C8b	1.8	15.9	0.26	24.4	3.7
C9a	5/1/18 10:00	6.1	15.9	2	45	C9A	2.470	C9A	1.81	3.76	C9a	3.7	16.4	0.2	73.1	3.5
C9b	5/1/18 10:21	6.03	12.7	2	30	C9B	0.646	C9B	-6.33	4.59	C9b	0.6	6.7	0.2	10.6	2.1
C10a	5/1/18 11:05	6.8	12.6	5	45	C10A	7.760	C10A	-1.46	5.69	C10a	6.9	3.4	0.76	9.5	3.2
C10b	5/1/18 11:12	6.63	12.4	20	30	C10B	15.606	C10B	3.03	5.99	C10b	31.3	2.0	3.91	83.8	3.8
C11a	5/1/18 11:46	6.93	14.6	0	45	C11A	0.000	C11A	--	--	C11a	0.8	9.0	0.41	40.2	1.6
C11b	5/1/18 11:52	6.75	13.9	1	30	C11B	0.119	C11B	6.10	12.32	C11b	0.9	6.7	1.08	61.7	2.4
C12a	5/1/18 12:41	6.8	14.1	0	32	C12A	0.000	C12A	--	--	C12a	1.7	0.9	1.22	130.0	1.8
C12b	5/1/18 12:47	7.08	13.5	0	20	C12B	0.000	C12B	--	--	C12b	1.3	0.9	1.51	154.0	12.8
C13a	5/1/18 13:30	6.7	13.7	0	45	C13A	0.000	C13A	--	--	C13a	0.6	6.5	0.26	43.4	0.9
C13b	5/1/18 13:39	7.12	13	0	30	C13B	0.000	C13B	--	--	C13b	1.3	7.3	1.32	130.0	1.1
D1a	5/1/18 14:19	7.03	14	0	45	D1A	0.000	D1A	--	--	D1a	0.5	7.7	0.26	39.2	2.0
D1b	5/1/18 14:26	6.83	15.5	0	30	D1B	0.000	D1B	--	--	D1b	0.8	4.9	0.68	70.5	0.6
D2a	5/1/18 15:00	7.56	14.3	5	45	D2A	1.652	D2A	17.09	8.63	D2a	17.3	44.3	U	26.6	1.2
D2b	5/1/18 15:06	6.47	14.1	50	30	D2B	13.455	D2B	6.94	0.88	D2b	38.8	90.1	1.33	31.2	0.7
D3a	5/1/18 15:41	6.39	14.5	20	45	D3A	8.983	D3A	1.07	0.47	D3a	31.5	25.5	0.85	28.4	4.3
D3b	5/1/18 15:48	6.12	13.5	50	30	D3B	13.142	D3B	1.46	1.57	D3b	34.4	2.6	1.12	32.4	1.1
D4a	5/1/18 16:19	7.87	15.2	20	45	D4A	10.238	D4A	1.33	-0.25	D4a	29.4	25.1	0.41	21.6	0.5

Field Measurements						University of Nebraska					EPA R5 Laboratory					
Sample_ID	SampleDate_Time	pH_SU	Water_Temperature_C	Nitrate_Field_Test_mgl	Sample_Depth_from_Surface_ft	Sample_ID	NO3+NO2-N	Sample_ID	15N-NO3	18O-NO3	Sample ID	Chloride (mg/L)	Sulfate (mg/L)	Ammonia-N (mg/L)	Iron (ug/l)	Manganese (ug/l)
D4b	5/1/18 16:26	6.51	14	50	30	D4B	17.697	D4B	1.64	-1.72	D4b	63.7	93.0	2.82	75.8	3.5
D5a	5/2/18 6:38	8.5	10.7	2	45	D5A	0.451	D5A	-0.79	4.94	D5a	1.7	10.3	0.5	58.9	4.84
D5b	5/2/18 6:46	6.66	10	2	30	D5B	1.175	D5B	-8.93	-4.10	D5b	0.8	6.7	0.23	27.5	2.88
D6a	5/2/18 7:17	8.23	12.4	50	45	D6A	41.140	D6A	-0.83	-2.95	D6a	45.7	96.9	0.49	30.3	0.66
D6b	5/2/18 7:29	7.35	12	50	30	D6B	24.537	D6B	-2.70	-0.51	D6b	27.9	67.0	0.67	43.8	1.26
D7a	5/2/18 8:12	8.18	12.9	50	45	D7A	30.701	D7A	-2.62	1.53	D7a	46.8	68.7	U	6.14	2.28
D7b	5/2/18 8:19	6.56	13.8	50	30	D7B	32.208	D7B	-4.99	-3.17	D7b	41.2	112.0	0.49	41.1	6.69
D8a	5/2/18 8:55	8.3	13.3	50	45	D8A	48.759	D8A	8.24	4.86	D8a	50.6	88.8	0.77	22.3	3.24
D8b	5/2/18 9:11	6.9	13.6	50	30	D8B	39.010	D8B	0.23	2.27	D8b	66.2	86.4	0.68	44.1	9.73
D9a	5/2/18 9:45	8.16	13.8	20	45	D9A	30.252	D9A	-1.65	1.23	D9a	41.4	71.0	0.21	19.3	1.03
D9b	5/2/18 9:54	7.39	12.7	5	30	D9B	1.521	D9B	2.72	1.35	D9b	4.9	10.8	0.34	31.7	2.13
D10a	5/2/18 10:29	8.69	15.5	20	45	D10A	8.794	D10A	-6.75	-3.01	D10a	22.8	28.9	0.22	36.3	1.97
D10b	5/2/18 10:41	6.67	14	20	30	D10B	8.403	D10B	-1.72	0.08	D10b	21.6	31.6	0.31	29.1	5
D11a	5/2/18 11:19	7.04	14.3	20	45	D11A	28.038	D11A	1.96	5.26	D11a	22.5	21.4	U	3.33	2.58
D11b	5/2/18 11:42	6.08	13.5	20	30	D11B	14.492	D11B	-4.92	3.11	D11b	34.9	60.6	U	4.03	2.27
E1a	5/2/18 12:41	8.09	13.5	20	45	E1A	11.656	E1A	3.35	6.17	E1a	33.2	76.3	U	11.6	4.35
E1b	5/2/18 12:58	6.36	13.3	50	30	E1B	11.808	E1B	6.84	5.39	E1b	27.3	38.0	1.02	30.7	5.08
E2a	5/2/18 13:28	8.66	13.8	2	45	E2A	0.995	E2A	2.63	6.36	E2a	29.0	8.5	U	8.17	2.46
E2b	5/2/18 13:37	6.87	12.6	2	30	E2B	2.579	E2B	1.89	-0.20	E2b	1.8	13.0	0.73	29.9	3.93
E3a	5/2/18 14:03	8.56	14.3	5	45	E3A	3.831	E3A	-0.03	1.74	E3a	2.0	46.7	0.21	24.8	2.01
E3b	5/2/18 14:09	8.11	12.7	5	30	E3B	6.140	E3B	0.68	1.59	E3b	1.0	27.4	0.35	31.6	2.68
E4a	5/2/18 14:37	7.2	17.5	20	45	E4A	26.056	E4A	3.69	5.12	E4a	16.4	71.0	0.87	45.7	1.25
E4b	5/2/18 14:43	6.82	14.3	20	30	E4B	19.956	E4B	-0.84	4.71	E4b	33.7	62.8	1.37	49.3	5.97
E5a	5/2/18 15:08	8.06	14	50	45	E5A	28.326	E5A	1.29	4.91	E5a	30.8	69.3	0.22	26.7	1.31
E5b	5/2/18 15:13	6.9	13.7	20	30	E5B	17.491	E5B	2.59	5.44	E5b	28.9	61.3	0.73	44.6	2.77
E6a	5/2/18 15:38	8.62	13.4	0	45	E6A	0.149	E6A	-6.39	3.20	E6a	0.5	6.0	0.26	15.1	1.64
E6b	5/2/18 15:44	6.47	12.6	0	30	E6B	0.093	E6B	-2.48	4.47	E6b	0.7	5.6	0.39	42.9	1.62
E7a	5/2/18 16:09	5.98	14.2	20	45	E7A	16.130	E7A	3.76	7.91	E7a	33.0	41.1	U	19.5	2.11
E7b	5/2/18 16:35	5.73	13.2	50	30	E7B	13.811	E7B	-4.23	-2.39	E7b	32.4	47.5	U	10.9	1.52
E10a	5/3/18 7:15	7.06	10.3	2	45	E10A	0.427	E10A	-4.15	2.91	E8a	26.9	34.6	U	12.6	0.18

Field Measurements						University of Nebraska					EPA R5 Laboratory					
Sample_ID	SampleDate_Time	pH_SU	Water_Temperature_C	Nitrate_Field_Test_mgl	Sample_Depth_from_Surface_ft	Sample_ID	NO3+NO2-N	Sample_ID	15N-NO3	18O-NO3	Sample ID	Chloride (mg/L)	Sulfate (mg/L)	Ammonia-N (mg/L)	Iron (ug/l)	Manganese (ug/l)
E10b	5/3/18 7:27	7.05	10	0	30	E10B	0.042	E10B	12.57	35.93	E8b	37.1	60.6	0.46	33.9	0.56
E8a	5/3/18 8:40	5.76	11.3	20	45	E8A	28.579	E8A	11.47	15.97	E10a	0.6	8.5	U	7.83	0.24
E8b	5/3/18 8:48	6.18	10.9	50	30	E8B	21.058	E8B	6.01	9.17	E10b	1.1	10.2	U	44.4	1.01
E9a	5/3/18 9:53	6.75	11	10	45	E9A	20.791	E9A	29.64	22.79	E9a	31.2	64.8	U	15.9	0.24
E9b	5/3/18 10:02	6.15	10.9	20	30	E9B	20.229	E9B	9.39	13.17	E9b	32.1	62.3	0.34	40.5	1.04